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ORIGINAL ARTICLE

Unsymmetrically urea silatranes: Synthesis, characterization and a selective on–off fluorescence response to acetate anion

Gurjaspreet Singh [a,*], Amandeep Saroa [a], Sunita Rani [a], Promila [a], Duane Choquesillo-Lazarte [b], Subash Sahoo [a]

[a] *Department of Chemistry, Panjab University, Chandigarh 160014, India*
[b] *Laboratorio de Estudios Cristalográficos, IACT, CSIC-University of Granada, Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain*

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Abstract New unsymmetrically Substituted Urea enclosed Silatranes (USUS) **2**–**5** are prepared in good yield by nucleophilic attack of pyrrolidine, piperidine, 3-methylpyridine-2-amine and N-methylbenzenamine containing active hydrogen atom on newly synthesized 3-isocyanatopropylsilatrane **1**. All the compounds have been characterized by elemental analysis, IR, multinuclear (^{1}H and ^{13}C) NMR and mass spectrometry. The single crystal X-ray crystallography technique facilitates the establishment of exact structures of silatranes **2**, **3** and **4**. The fluorescence titration results have revealed a selective on–off fluorescence response of silatranes toward acetate anion.

1. Introduction

Silatranes i.e. cyclic organosilicon ethers of tris(2-oxyalkyl)amines and their derivatives compose a class of neutral pentacoordinate silicon compounds by notable feature of the transannular interaction between the silicon center and the nitrogen atom. Several review articles with special emphasis on synthesis, structure, reactivity and biological activities of silatranes have been reported (Verkade, 1994; Chuit et al., 1993; Voronkov et al., 2012). Due to their verified antiviral, anti-inflammatory, anticancer and antitumor activities, seed germination effects and agricultural applications, silatranes are broadly used in biological systems (Puri et al., 2011). To further enhance the appliance of silatranes in the biological and material science, modification of silatrane at the exocyclic position is highly encouraged (Singh et al., 2012, 2014a, 2014b).

An unsymmetrically substituted urea is a common structural feature of many biologically active compounds such as enzyme inhibitors and pseudopeptides and consequently, it actively participates in herbicidal, inhibition of nitric oxide, and anti-microbial, anti-HIV, anti-viral, and analgesic

* Corresponding author. Tel.: +91 172 2534428, +91 9814302099.
E-mail address: gjpsingh@pu.ac.in (G. Singh).
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activities (Sivan et al., 2013; Vega-Perez et al., 2012; Sharma et al., 2013). Urea functionality is generated conveniently by the reactions of isocyanate group with amines having active hydrogen atom (Sandler and Karo, 1971). Prompted by these particulars about urea compounds, we have attempted the synthesis of USUS **2**–**5** by conventional method in this manuscript.

The recognition and sensing of anions has become an important aspect of supramolecular chemistry. This is due to the role of these ions in physiology and in the environment. The urea groups have been focused as anion binding sites, owing to their hydrogen-bonding ability that results in the formation of quite stable complexes bonded strongly with biologically important anions such as acetate, phosphate or chloride (Bondy and Loeb, 2003; Kim et al., 2006). The easy synthesis of urea allied compounds using commercially available reagents and following a single-step procedure is an additional benefit for researchers working in the field of chemosensing. Therefore, a variety of receptors containing one or more urea subunits have been designed and tested for anion recognition and sensing over the past few years (Okudan et al., 2013; Kondo et al., 2011a,b). Keeping this in mind, we have studied the anion sensing ability of USUS having hydrogen-bond donor tendency using fluorescence technique.

2. Experimental section

2.1. Materials and methods

2.1.1. Synthesis and characterization

3-Isocyanatopropyltriethoxysilane and triethanolamine were purchased from Sigma–Aldrich. Pyrrolidine (CDH), piperidine (SDFCL), 3-methylpyridine-2-amine (Aldrich) and N-methylbenzenamine (CDH) were refluxed over KOH pellets and vacuum distilled before use. All operations were carried out under a dry nitrogen atmosphere using Schlenk line. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using 400 MHz (Bruker Avance II 400) FT NMR instrument. Infrared spectra were obtained with a Thermo Nicolet Nexus 670 spectrometer. C, H and N analyses were performed on a FLASH-2000 organic element analyzer while Si content was estimated gravimetrically. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. Fluorescence spectroscopy was performed on Perkin Elmer LS 55 Fluorescence Spectrometer.

2.1.2. X-ray crystallography

Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Suitable crystals were mounted on MiTeGenMicromounts™ and these samples were used for data collection. Data were collected with a BrukerD8 Venture (100 K) diffractometer. The data were processed with APEX2 (BRUKER, APEX2 Software, 2013) program and corrected for absorption using SADABS (Sheldrick, 2009). The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full-matrix least-square procedure using anisotropic displacement parameters (Sheldrick, 2008). All hydrogen atoms were located in different Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. Geometric calculations were carried out with PLATON (Spek, 2010) and drawings were produced with Olex2 (Dolomanov et al., 2009) and MERCURY (Macrae et al., 2008).

2.2. Syntheses

2.2.1. 1-(3-Isocyanatopropyl)-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecane (3-isocyanatopropylsilatrane, 1)

A two-necked round bottomed flask outfitted with a magnetic stirrer and Dean-Stark apparatus was sequentially charged in a stream of nitrogen with 3-isocyanatopropyltriethoxysilane (1.00 mL, 4.04 mmol) dissolved in 30 mL dry toluene. The tetradentate ligand triethanolamine (0.53 g, 4.04 mmol) was added slowly to the solution and allowed to stir at 25 °C for 10 min in the presence of catalytic amount of sodium ethoxide. The mixture was refluxed for 4 h and solvent was removed under reduced pressure. The white colored oil was obtained. Yield: 0.82 g (82%). IR (cm^{-1}) = 605 m (ν N → Si), 1089 s (ν Si—O), 2227 s (ν N═C═O), 2884, 2947 m (ν CH_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.38 (t, 2H, J = 8.4 Hz, $SiCH_2$), 1.57 (m, 2H, CCH_2C), 2.59 (t, 4H, J = 6.8 Hz, CH_2N), 2.67 (t, 6H, J = 5.7 Hz, NCH_2), 3.61 (t, 6H, J = 5.7 Hz, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.31 ($SiCH_2$), 24.27 ($C\boldsymbol{C}H_2C$), 42.97 ($C\boldsymbol{C}H_2N$), 51.83 (NCH_2), 56.84 (OCH_2), 123.81 (N═C═O). MS: m/z (relative abundance (%), assignment) = 132 [13.7, ($HSi(OCH_2CH_2)_2NH^+$], 150 [11.46, ($HOCH_2CH_2)_3$ NH^+], 174 [23.5, $Si(OCH_2CH_2)_3N^+$], 192 [35.8, $Si(OCH_2CH_2)_3N^+ \cdot NH_3$], 259 [100, $(M + H)^+$], 281 [42.7, $(M + Na)^+$].

General procedure for the preparation of unsymmetrically substituted urea silatranes (2–5)

3-Isocyanatopropylsilatrane **1** (3.01 mmol) was dissolved in chloroform and a solution of substituted amine (3.01 mmol) in 20 mL chloroform was added dropwise with stirring. The mixture was stirred and refluxed for 4 h. Upon cooling, the solvent was evaporated under vacuum and the solid compounds **2**–**5** were extracted by adding hexane.

2.2.2. N-(3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecan-1-yl)propyl)pyrrolidine-1-carb-oxamide (USUS 2)

The reaction of 3-isocyanatopropylsilatrane **1** (1.00 g, 3.87 mmol) with secondary amine pyrrolidine (0.31 mL, 3.87 mmol) resulted in USUS **2** as a white colored solid. The crystals of **2** were grown in chloroform-hexane mixture (3:1). Yield: 1.02 g (80%). M.p.: 134–136 °C. Anal. Calcd. for $C_{14}H_{27}N_3O_4Si$ (329): C, 51.04; H, 8.26; N, 12.75; Si, 8.52. Found: C, 50.90; H, 7.87; N, 12.41; Si, 8.42. IR (cm^{-1}) = 590 m (ν N → Si), 1095 s (ν Si—O), 1654 s (ν C═O), 2881, 2950 m (ν CH_2), 3285 m (ν NH). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.25 (t, 2H, J = 8.4 Hz, $SiCH_2$), 1.19 (t, 4H, J = 6.8 Hz, CH_2N), 1.54 (m, 2H, CCH_2C), 2.62 (t, 6H, J = 5.7 Hz, NCH_2), 2.94 (m, 4H, CH_2N), 3.02 (q, 4H, J = 6.8 Hz, CH_2CH_2), 3.52 (t, 6H, J = 5.7 Hz, OCH_2), 5.76 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.49 ($SiCH_2$), 24.13 ($C\boldsymbol{C}H_2C$), 25.15 (CH_2), 43.56 ($C\boldsymbol{C}H_2N$), 44.23 ($\boldsymbol{C}H_2N$), 50.22 (NCH_2), 56.91 (OCH_2), 157.44 (C═O). MS: m/z (relative abundance (%), assignment) = 132 [17.7,

($HSi(OCH_2CH_2)_2NH^+$], 150 [5.8, ($HOCH_2CH_2)_3$ NH^+], 174 [6.3, $Si(OCH_2CH_2)_3N^+$], 192 [7.8, $Si(OCH_2CH_2)_3N^+ \cdot NH_3$], 330 [100, $(M + H)^+$], 352 [6.8, $(M + Na)^+$].

2.2.3. N-(3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecan-1-yl)propyl)piperidine-1-carbo-xamide (USUS 3)

The reaction of 3-isocyanatopropylsilatrane **1** (1.00 g, 3.87 mmol) with secondary amine piperidine (0.38 mL, 3.87 mmol) resulted in USUS **3** as white colored solid. The crystals of **3** were grown in chloroform-hexane mixture. Yield: 1.10 g (83%). M.p.: 141–143 °C. Anal. Calcd for $C_{15}H_{29}N_3O_4Si$ (343): C, 52.45; H, 8.51; N, 12.23; Si, 8.18. Found: C, 52.31; H, 8.44; N, 12.15; Si, 8.11. IR (cm^{-1}) = 595 m (ν N → Si), 1053 s (ν_s Si—O), 1651 s (ν C═O), 2839, 2935 m (ν CH_2), 3289 m (ν NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.38 (t, 2H, J = 8.4 Hz, $SiCH_2$), 1.17 (m, 6H, CH_2CH_2), 1.53 (m, 2H, CH_2), 2.72 (t, 6H, J = 5.7 Hz, NCH_2), 2.94 (t, 2H, J = 7.1 Hz, CH_2N), 3.02 (q, 4H, J = 6.8 Hz, CH_2NH), 3.52 (t, 6H, J = 5.7 Hz, OCH_2), 5.76 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.87 ($SiCH_2$), 25.05 (CCH_2C), 25.92, 26.13 (pip-CH_2), 43.55 (CCH_2N), 45.07 (pip-CH_2N), 50.03 (NCH_2), 56.91 (OCH_2), 156.53 (C═O). MS: *m*/*z* (relative abundance (%), assignment) = 132 [9.3, ($HSi(OCH_2CH_2)_2$ NH^+], 150 [14.2, ($HOCH_2CH_2)_3$ NH^+], 174 [12.4, $Si(OCH_2CH_2)_3N^+$], 192 [15.7, $Si(OCH_2CH_2)_3N^+ \cdot NH_3$], 344 [5.6, $(M + H)^+$], 366 [100, $(M + Na)^+$].

2.2.4. 3-(3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecan-1-yl)propyl)-1-methyl-1-phenyl urea (USUS 4)

The reaction of 3-isocyanatopropylsilatrane **1** (1.00 g, 3.87 mmol) with N-methylbenzenamine (0.50 mL, 3.87 mmol) resulted in USUS **4** as white colored solid. Yield: 1.05 g (74%). M.p.: 171–173 °C. Anal. Calcd for $C_{17}H_{27}N_3O_4Si$ (365): C, 55.86; H, 7.45; N, 11.50; Si, 7.68. Found: C, 55.62; H, 7.35; N, 11.31; Si, 7.53. IR (cm^{-1}) = 592 m (ν N → Si), 1093 s (ν Si—O), 1652 s (ν C═O), 2883, 2941 m (ν_s CH_2), 3287 m (ν NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.31 (t, 2H, J = 8.4 Hz, $SiCH_2$), 1.64 (m, 2H, CH_2), 2.78 (t, 6H, J = 5.7 Hz, NCH_2), 3.15 (s, 3H, NCH_3), 3.41 (q, 2H, J = 6.8 Hz, CH_2NH), 3.61 (t, 6H, J = 5.7 Hz, OCH_2), 5.49 (s, 1H, NH), 7.19–7.39 (m, 4H, Ar—H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.04 ($SiCH_2$), 25.55 (CCH_2C), 36.73 (NCH_3), 43.40 (CCH_2N), 50.07 (NCH_2), 56.78 (OCH_2), 125.58–144.05 (Ar—C), 156.54 (C═O). MS: *m*/*z* (relative abundance (%), assignment) = 132 [16.3, ($HSi(OCH_2CH_2)_2NH^+$], 150 [14.9, ($HOCH_2CH_2)_3$ NH^+], 174 [19.6, $Si(OCH_2CH_2)_3N^+$], 192 [38.5, $Si(OCH_2CH_2)_3N^+ \cdot NH_3$], 366 [100, $(M + H)^+$].

2.2.5. 1-(3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecan-1-yl)propyl)-3-(3-methylpyridin-2-yl)urea (USUS 5)

The reaction of 3-isocyanatopropylsilatrane **1** (1.00 g, 3.87 mmol) with primary amine 3-methylpyridin-2-amine (0.39 mL, 3.87 mmol) resulted in USUS **5** as cream colored solid. Yield: 0.98 g (69%). M.p.: 184–186 °C. Anal. Calcd for $C_{16}H_{26}N_4O_4Si$ (366): C, 52.44; H, 7.15; N, 15.29; Si, 7.66. Found: C, 52.24; H, 7.03; N, 15.16; Si, 7.51. IR (cm^{-1}) = 598 - m (ν N → Si), 1088 s (ν Si—O), 1658 s (ν C═O), 2879, 2939 m (ν CH_2), 3291 m (ν NH). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.23 (t, 2H, J = 8.4 Hz, $SiCH_2$), 1.41 (m, 2H, CCH_2-C), 2.78 (t, 6H, J = 5.7 Hz, NCH_2), 3.15 (s, 3H, CH_3), 3.41 (t, 2H, J = 8.2 Hz, CCH_2N), 3.61 (t, 6H, J = 5.7 Hz, OCH_2), 3.78 (s, 1H, NH), 5.49 (s, 1H, NHAr), 7.19–7.39 (m, 4H, Ar—H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.13 ($SiCH_2$), 25.55 (CCH_2C), 42.57 ($ArCH_3$), 43.93 (CCH_2N), 50.09 (NCH_2), 56.86 (OCH_2), 128.05–144.94 (Ar—C), 154.68 (C═O). MS: *m*/*z* (relative abundance (%), assignment) = 132 [16.4, ($HSi(OCH_2CH_2)_2NH^+$], 150 [18.6, ($HOCH_2CH_2)_3$ NH^+], 174 [29.2, $Si(OCH_2CH_2)_3N^+$], 192 [40.9, $Si(OCH_2$-$CH_2)_3N^+ \cdot NH_3$], 367 [100, $(M + H)^+$].

2.3. Fluorescence titration

All titration experiments were performed on 2.5×10^{-5} M solutions of compounds **2**, **3**, **4** and **5** in CH_3CN. Typically, aliquots of freshly prepared Bu_4NX (X = F^-, Cl^-, Br^-, and CH_3COO^-) standard solutions (10^{-3} M in CH_3CN) were added and the fluorescence spectra of the samples were recorded.

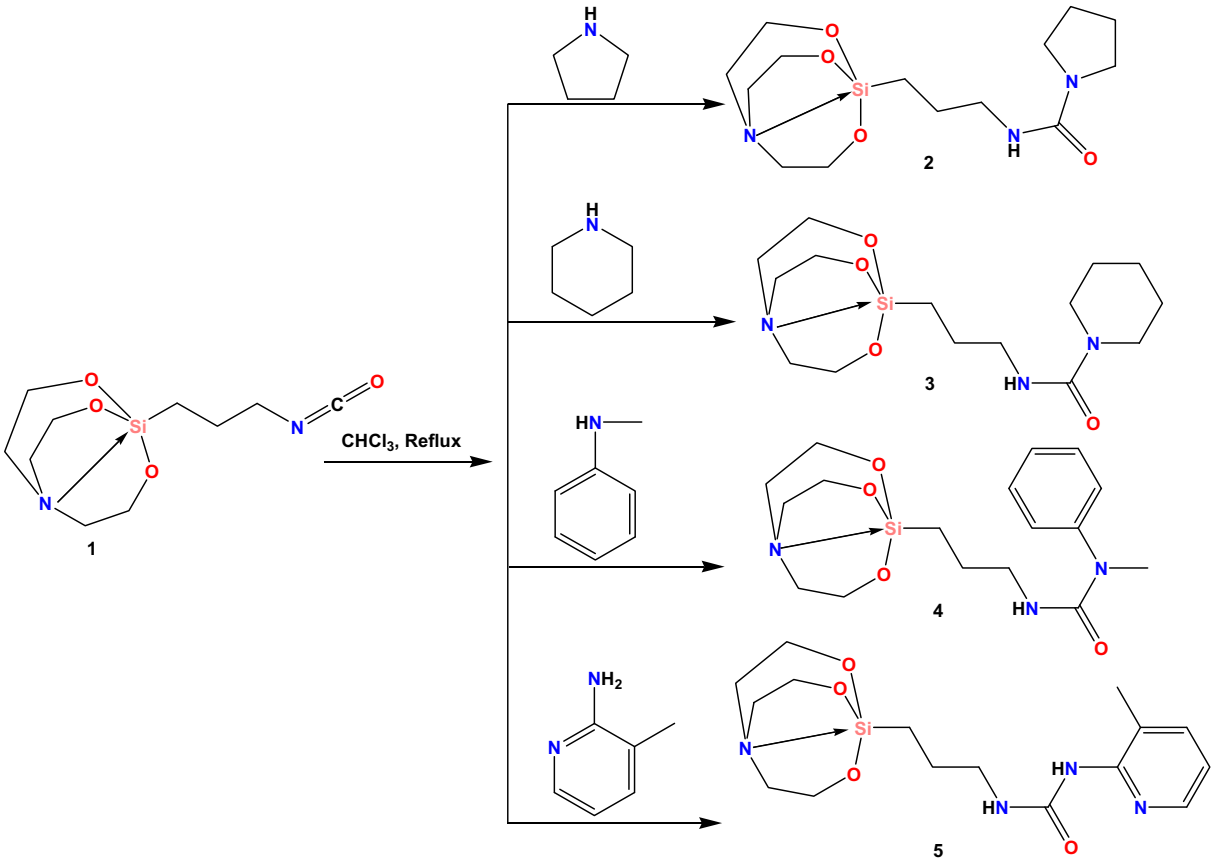
3. Results and discussion

3.1. Synthesis

A conventional method for the synthesis of substituted urea involves reaction of alkyl isocyanates with primary or secondary amines in organic solvents. The reactions of isocyanates with amines, having active hydrogen, are key reactions of isocyanate chemistry. A qualitative consideration of resonance hybrid structures of isocyanates indicates that the electron density is greatest on oxygen due to highest net negative charge and least on carbon with highest net positive charge, the nitrogen atom being intermediate with a net negative charge. The reactions of isocyanates with active hydrogen compounds involve attack by a nucleophilic center (nitrogen atom in case of primary/secondary amines and oxygen atom in alcohols) upon the electrophilic carbon of the isocyanates. Using conventional method, the unsymmetrically substituted urea functionalized silatranes **2–5** were synthesized by the rearrangement reaction of 3-isocyanatopropylsilatrane **1** and amines viz. pyrrolidine, piperidine, N-methylbenzenamine and 3-methylpyridine-2-amine as shown in Scheme 1 without any catalyst. The organosilicon isocyanates readily react with amines in a highly exothermic way. The reaction conditions are refluxing the mixture of 3-isocyanatopropylsilatrane with primary/secondary amines in chloroform at 80 °C for 4 h.

3.2. Spectroscopic studies

FT-IR Spectra for all silatranes were recorded as neat spectra in the range of 4000–400 cm^{-1}. The presence of symmetric deformational vibration peak of the silatranyl skeleton possessing transannular N → Si bond is observed in the region 610–570 cm^{-1} for all silatranes. The Si—O stretching vibration is assigned to the bands present in 1100–1075 cm^{-1}. The absorption band assigned in the range of 1550–1520 cm^{-1} is indicated for HN—C(═O). IR spectra exhibit characteristic absorption bands of >C═O in the region of 1660–1625 cm^{-1} for unsymmetrically substituted urea silatranes,



Scheme 1 Synthesis of unsymmetrically substituted urea functionalized silatranes **2–5**.

which are detected at relatively low values due to weakening of C═O bond by resonance involved in NHC(═O)NH moiety. The stretching vibrations of methylene and methyl groups are appeared in the region 3000–2800 cm^{-1}. The asymmetric and symmetric NH stretching modes are assigned to the region 3400–3200 cm^{-1}.

The NMR spectroscopic (^{1}H and ^{13}C) data, recorded at room temperature, for all compounds are consistent with the structure of the synthesized products. In ^{1}H NMR spectra, an upfield triplet appears for the methylene group attached to the silicon atom i.e. $SiCH_2$ for all silatranes due to increased electron density on silicon atom due to silatranyl skeleton. The C***C***H_2C proton of propyl chain resonances split up into a multiplet due to coupling with adjacent methylene protons and appeared in region of $\delta \approx 1.45$–1.60 ppm. The CC***H***$_2$N protons are confirmed by quartet due to coupling of adjacent methylene protons and NH group in the region of 3.02–3.60 ppm, and the exact value is seen to depend upon exocyclic group attached. The silatranes possessing $Si(OCH_2CH_2)_3N$ silatranyl moiety consist of two intense triplets due to NCH_2 ($\delta \approx 2.75$–2.90 ppm) and OCH_2 protons ($\delta \approx 3.65$–3.80 ppm) as depicted. The NH proton attached to propyl chain is observed as a broad singlet peak in the region of 4.20–5.50 ppm. In ^{1}H NMR spectrum, methylene protons attached to nitrogen of pyrrolidine and piperidine appear as triplets in region of 2.94–3.05 ppm and other methylene protons appear as multiplets due to adjoining methylene carbon in the range of 1.19–1.23 ppm for compounds **2** and **3**. The methyl group attached to secondary amine nitrogen and directly to aromatic ring appears at 3.15 and 2.75 ppm in case of compounds **4** and **5** respectively. The aromatic protons are observed in the range 7.19–7.39 ppm.

In ^{13}C NMR spectra, the methylene carbon of propyl chain attached to silicon atom is appeared as the most shielded carbon atom which is observed around $\delta \approx 12.50$–14.20 ppm for all silatranes. The peak due to C***C***H_2C is observed in the region $\delta \approx 24.00$–25.50 ppm. The peak for C***C***H_2N is revealed with large variation in the region $\delta \approx 42.00$–50.13 ppm, certainly depending upon the exocyclic moiety. The silatranes possessing $Si(OCH_2CH_2)_3N$ show two peaks in the region $\delta \approx 51.00$–55.50 and $\delta \approx 56.50$–58.50 ppm which are assigned to silatranyl NCH_2 and OCH_2 respectively. All unsymmetrically substituted urea and carbamate silatranes exhibit less shielded carbonyl carbon in the region 155.23–157.56 ppm.

The mass spectra of all silatranes show general characteristics of silatrane fragmentation pattern. All silatranes demonstrate their respective molecular ion peaks along with peaks corresponding to addition of H, Na and K. Besides the molecular ion peak, a peak corresponding to 1-propylsilatranyl ion (m/z = 216) is observed upon the cleavage of γ-carbon of propyl chain. Further, it loses one of the OCH_2CH_2 arms to form bicyclic fragment (m/z = 172). Homolytic cleavage of Si-CH_2 results in a silatranyl fragment with direct Si—N covalent bond (m/z = 174). It is noteworthy that the molecular ion peak is more abundant as compared to silatranyl ion peak. This

silatranyl fragment (m/z = 174) further loses a cyclic arm to form bicyclic moiety (m/z = 132). A very intense peak due to protonated triethanolamine (m/z = 150) is observed along with an abundant peak at m/z = 192 that is attributed to the formation of silatranyl adduct with NH_3 for all silatranes.

3.3. X-ray diffraction studies

Single crystal X-ray diffraction study on the three compounds showed that molecules **2** and **3** crystallize in a monoclinic crystal system (space group = $P2_1/c$) while molecule **4** in orthorhombic crystal system (space group = $P2_12_12_1$). The ORTEP plots of all three compounds are shown in (thermal ellipsoids drawn at 50% probability) Fig. 1. Details of data collection and structure refinement, and selected bond lengths and angles of all the three compounds are listed in Table 1 and supporting data Table 1 respectively. All the three compounds possess usual silatrane skeleton containing Si atom in distorted trigonal bipyramidal geometry where coordination of tripodal trianionic $N(CH_2CH_2O—)_3$ entities acts as tetradentate coordinating unit each to Si to form five membered rings, so that a trans Si—N bond is formed. Due to this bond, Si achieves a coordination number of five with trigonal bipyramidal geometry. The O atoms of the tripodal trianionic unit occupy equatorial positions and the N donor is present at apical site

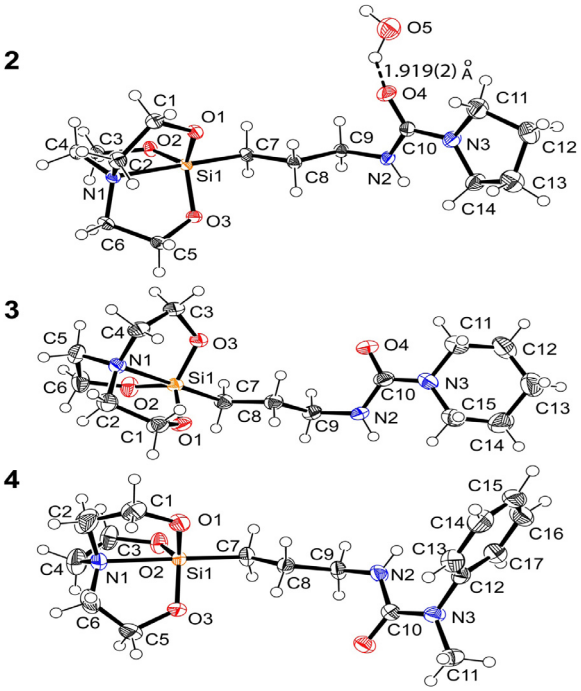


Figure 1 ORTEP plots of **1**, **2** and **3** (thermal ellipsoids drawn at 50% probability).

Table 1 Crystal data and structure refinement for compounds **2**, **3** and **4**.

Compound	**2**	**3**	**4**
Empirical formula	$C_{14}H_{29}N_3O_5Si$	$C_{15}H_{29}N_3O_4Si$	$C_{17}H_{27}N_3O_4Si$
Formula weight	347.49	343.5	365.51
Temperature (K)	150	150	149.9
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions (Å)	a = 9.3524(18)	a = 9.743(3)	a = 9.9060(11)
	b = 9.0436(9)	b = 8.7862(14)	b = 10.3075(7)
	c = 20.527(2)	c = 20.471(4)	c = 17.9801(11)
	β = 94.918(7)°	β = 94.249(13)°	$\alpha = \beta = \gamma$ = 90°
Volume (Å^3)	1729.8(4)	1747.6(7)	1835.9(3)
Z	4	4	4
Density (calculated), Mg/m^3	1.334	1.306	1.322
Absorption coefficient, mm^{-1}	0.164	0.158	0.155
F(000)	752	744	784
Crystal size (mm^3)	0.1 × 0.1 × 0.1	0.1 × 0.08 × 0.08	0.08 × 0.08 × 0.07
Theta range for data collection	2.32–26.37°	2.52–25.03°	2.27–26.34°
Index ranges	$-11 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 11$	$-12 \leqslant h \leqslant 12$
	$-11 \leqslant k \leqslant 11$	$-9 \leqslant k \leqslant 10$	$-12 \leqslant k \leqslant 12$
	$-25 \leqslant l \leqslant 25$	$-24 \leqslant l \leqslant 24$	$-22 \leqslant l \leqslant 22$
Reflections collected	9431	8683	21,154
Independent reflections	3516 [R(int) = 0.0399]	3078 [R(int) = 0.0459]	3759 [R(int) = 0.0631]
Completeness to theta	99.2	99.5	100
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6191	0.7452 and 0.6090	0.7456 and 0.5939
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3516/0/211	3078/0/208	3759/0/227
Goodness-of-fit on F^2	1.031	1.048	1.075
Final R indices [I > 2 sigma(I)]	R_1 = 0.0417	R_1 = 0.0550	R_1 = 0.0488
	wR_2 = 0.1000	wR_2 = 0.1419	wR_2 = 0.1314
R indices (all data)	R_1 = 0.0543	R_1 = 0.0774	R_1 = 0.0570
	wR_2 = 0.1060	wR_2 = 0.1547	wR_2 = 0.1376
Largest diff. peak and hole, e Å^{-3}	0.352 and −0.286	0.733 and −0.250	0.764 and −0.357

Table 2 Hydrogen bonding parameters for **2**, **3** and **4** (Å and °).

Compd	D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)	Symmetry transformations
2	N(2)—H(2)···O(3)#1	0.88	2.11	2.9000(19)	148.3	$-x+2, -y+2, -z+$
	O(5)—H(5C)···O(4)#2	0.87	1.92	2.782(2)	171.0	$-x+1, -y+2, -z+1$
	O(5)—H(5D)···O(2)#3	0.87	2.02	2.8674(19)	165.2	$x-1/2, -y+3/2, z+1/2$
3	N(2)—H(2)···O(3)#1	0.88	2.13	2.933(3)	152.3	$-x+1, -y+1, -z+2$
4	N(2)—H(2)···O(2)#1	0.88	2.49	3.172(3)	134.6	$-x+1, y-1/2, -z+1/2$

opposite to the urea-functionalized alkyl moiety. Among various variable parameters of the geometry around Si center, one of interest is the Si—N bond lengths, which are 2.143(1), 2.173(3) and 2.156(2) Å for **2**, **3**, and **4** respectively. Similarly, the bond angles N—Si—C_{ax} are found to be 178.64(7), 178.00(1) and 178.79(1)° for **2**, **3** and **4** respectively. All the Si—N bonds and angles around Si are within the range of reported values (Singh et al., 2014a,b). Again the existing —CH_2—CH_2—CH_2— alkyl chain between the urea moiety and Si center decreases the possible effect of —NHCONH— on the Si—N bonds and overall geometry. All the complexes are monomeric in nature with a slightly distorted (τ 0.99–1.0) trigonal bipyramidal (TBP) geometry around the Si atom specially for **2** and **3**. The distortion parameter $\tau = (\beta - \alpha)/60$ was calculated from the structural data where the value of τ should be 0 for perfect square-pyramidal geometry and 1 for a perfect TBP structure and is applicable to five-coordinate structures as an index of the degree of trigonality (Addison et al., 1984).

It is clear that all the structures are differing by their urea attached moiety which actually play an important role for overall molecular interactions and lattice arrangement. Among the various types of molecular interactions, —NH···O type is most common for all the three structures with value of 2.900(2), 2.933(3) and 3.172(3) for molecules **2**, **3** and **4** respectively (Table 2). From the values it is clear that the —NH···O type interaction is strongest in case of **2** and least in **4** (Fig. 2). There is a water molecule as lattice solvent in complex **2** where it is strongly H-bonded via —OH···O interactions and forces the two molecules to stay in a *T*-type fashion. A simplifier model for lattice arrangement is shown with each lattice structure (Fig. 3). It is clear that both molecules **2** and **3** have similar arrangement along *bc*-plane; however, there is compact paring alignment in **3** than in **2**. In case of **4**, the arrangement is totally different along *bc*-plane, where molecules prefer to lie on a head-to-head paring fashion in alternative line arrangement (Fig. 3).

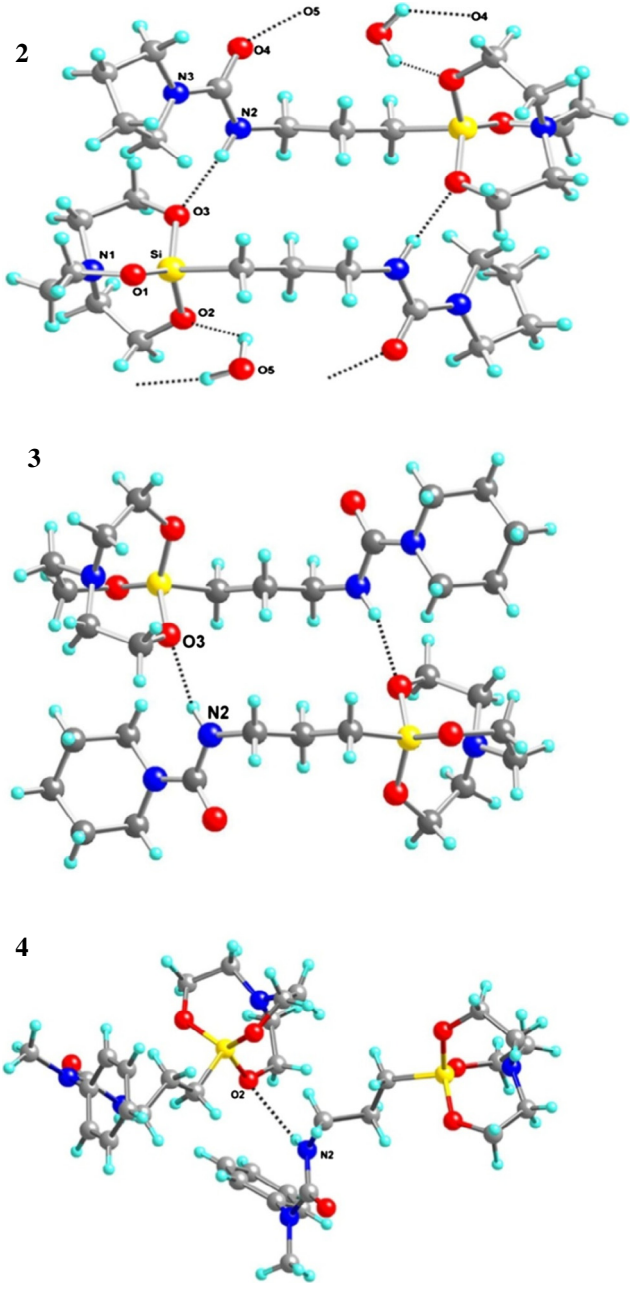


Figure 2 Molecular interactions via —NH···O for **2**, **3** and **4**.

3.4. Fluorescence titration

The fluorescence emission spectra of **2**, **3**, **4** and **5** were observed at 375, 383, 414 and 467 nm credited to substituted urea group by excitation at 331, 350, 360 and 464 nm in CH_3-CN. The anion sensing ability of the compounds **2**, **3**, **4** and **5** with different anions as tetrabutylammonium salts was investigated through fluorescence emission in CH_3CN. The fluorescence spectra of all the silatranes changed noticeably when small amount of AcO^- ions was added whereas none of the other anions (F^-, Cl^- and Br^-) produce any noticeable change in the emission spectra as shown in Fig. 4 for compound **5**. These silatrane based receptors have shown strong binding to acetate over other ions such as F^-, Cl^- and Br^-. The titra-

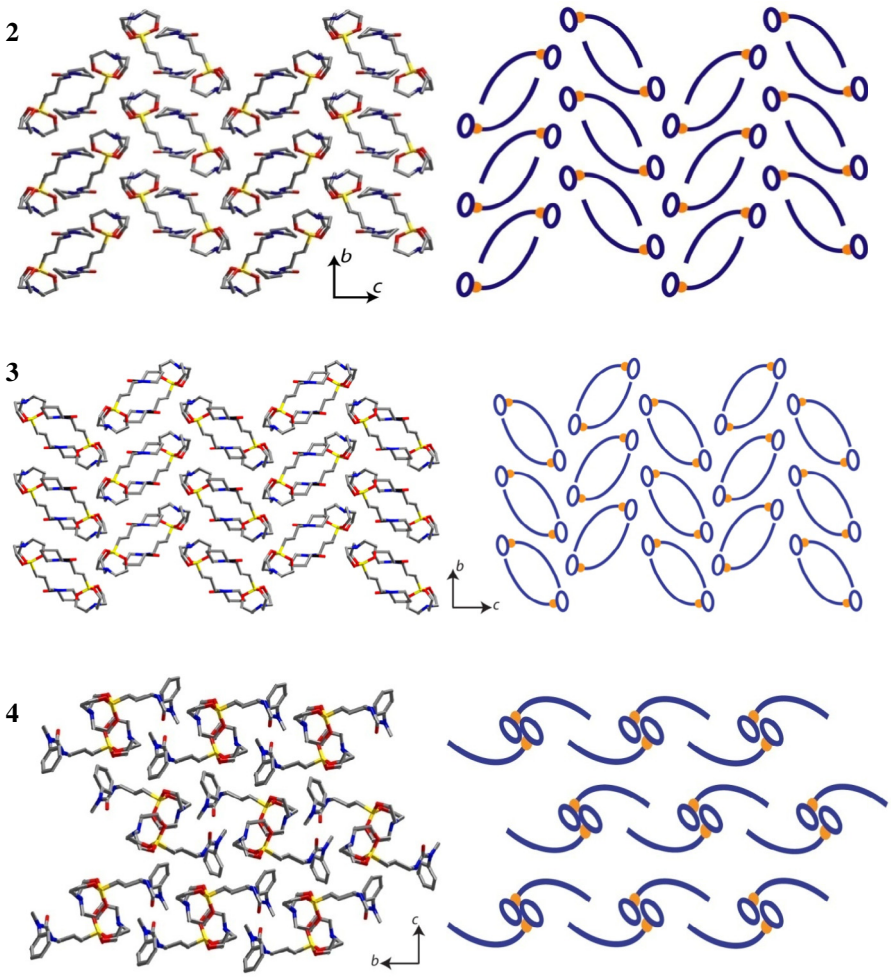


Figure 3 Lattice arrangement along *bc*-plane for compounds **2**, **3** and **4**.

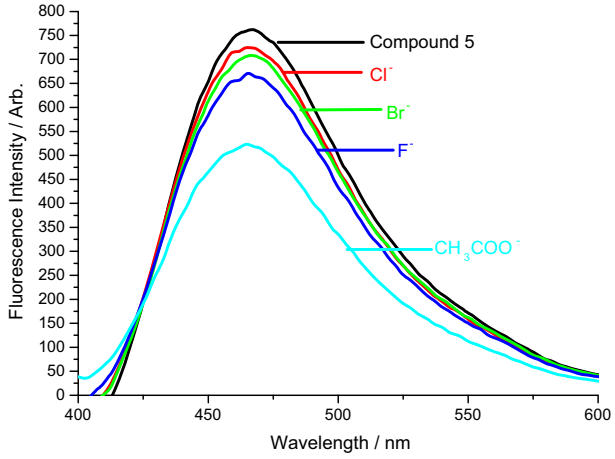


Figure 4 Fluorescence emission spectra for compound **5** in the presence of tetrabutylammonium salt of CH_3COO^-, F^-, Cl^- and Br^-.

tion is performed using 2.5×10^{-5} M solution of compounds **2**–**5** in CH_3CN with 15 equiv of AcO^-. In Fig. 5, the emissions were switched off or quenched, due to the formation of anion receptor hydrogen bonded complexes for all silatranes upon addition of CH_3COO^- ions (Kondo et al., 2011a,b). It is noteworthy that the fluorescence intensity of substituted phenyl urea silatranes **4** and **5** is higher than that of substituted urea silatranes **2** and **3** and it may be due to phenyl ring conjugation. The fluorescence intensity of **4** and **5** was decreased much with a slight bathochromic shift upon addition of AcO^- ions in CH_3CN. The high fluorescence intensity and significant spectral changes of **4** and **5** provide simple and effective fluorescence anion sensors.

4. Conclusions

We have successfully synthesized unsymmetrically substituted urea enclosed silatranes in good yield having good solubility in organic solvents and stability. Further, these silatranes have been exploited for fluorescence activity toward anion due to the presence of urea group possessing hydrogen bonding ability. The synchronization of silatranyl and urea moieties can facilitate numerous of applications in sol–gel processes, biological systems polymer chemistry and various commercial products.

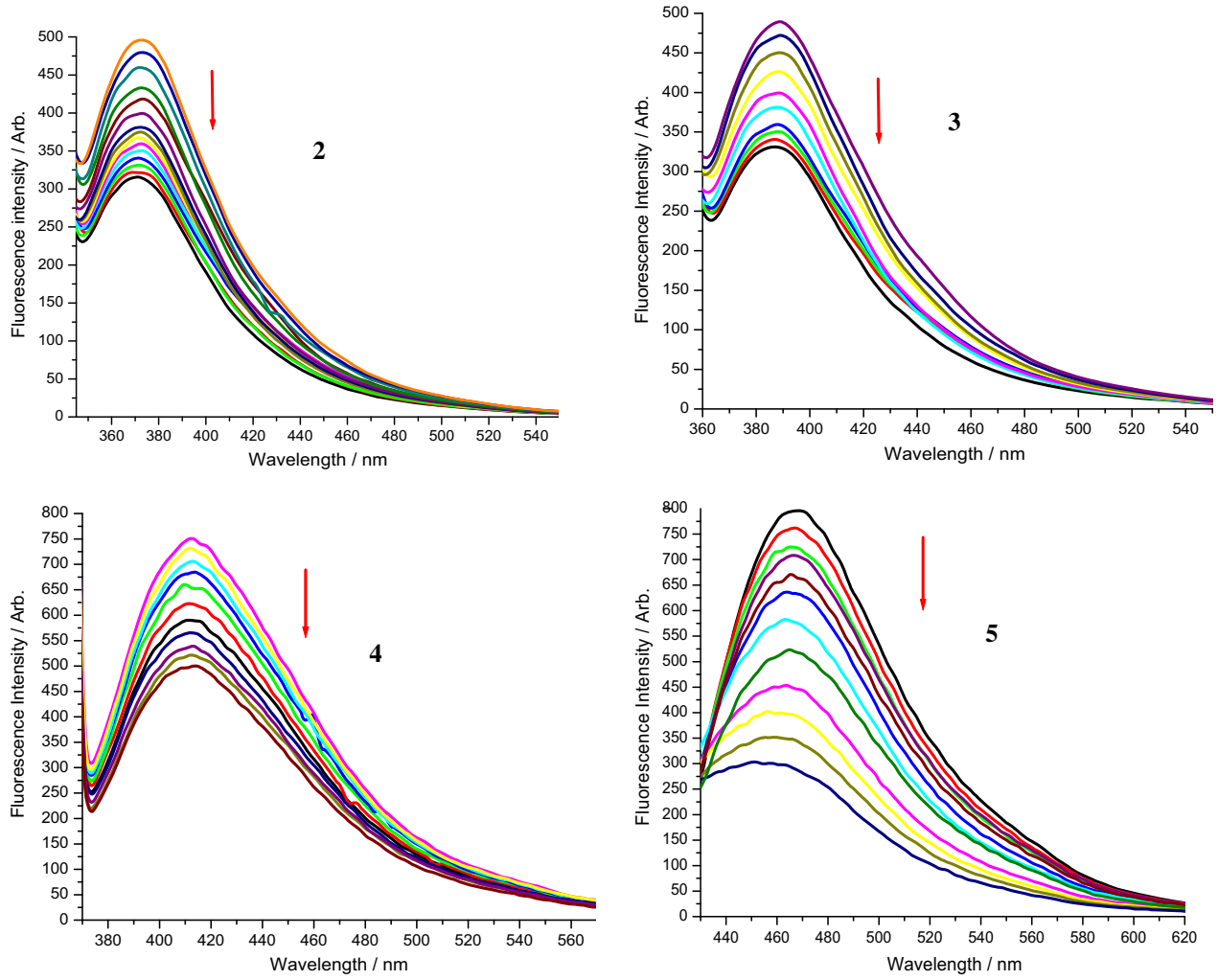


Figure 5 Fluorescence emission spectra for compounds **2**, **3**, **4** and **5** (2.5×10^{-5}) upon addition of 15 equiv acetate ion in CH_3CN at room temperature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2015.07.017.

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